Thermodynamics: Classical to Statistical

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Lecture - 20

Grand canonical distribution; Introduction to microcanonical ensemble

In grand canonical distribution we know

$$p_{Nj} = \frac{e^{-\beta E_{Nj}(V)}\, e^{-\gamma N}}{\Theta\,(V,T,\gamma)}$$

The grand canonical partition function, $\Theta\,(V,T,\gamma) = \sum_N \sum_j e^{-\beta E_{Nj}(V)} e^{-\gamma N}$

. Since, we obtained the partition function we can calculate different thermodynamical properties like average energy.

$$<E> = \sum_N \sum_j \; p_{Nj}(V,\beta,\gamma)\, E_{Nj}(V)$$

$$<E> = -\left(\frac{\partial \ln \Theta}{\partial \beta}\right)_{V,\gamma} = k_B T^2 \left(\frac{\partial \ln \Theta}{\partial T}\right)_{V,\gamma}$$

. We can also calculate average pressure.

$$<P> = \frac{1}{\Theta} \sum_N \sum_j \left(\frac{\partial E_{Nj}}{\partial V}\right) e^{-\beta E_{Nj}(V)} e^{-\gamma N}$$

$$\Rightarrow \quad <P> = k_B T \left(\frac{\partial \ln \Theta}{\partial V}\right)_{\beta,\gamma}$$

We can also calculate the average number of particles in a given system

$$<N> = \frac{1}{\Theta} \sum_N \sum_j \; N e^{-\beta E_{Nj}(V)} e^{-\gamma N}$$

$$\Rightarrow \quad <N> = \left(\frac{\partial \ln\Theta}{\partial\gamma}\right)_{V,\beta}$$

Now we can calculate other thermodynamical properties but before that what is the value of gamma we need to calculate next?

Let us consider a function

$$f\,(\beta, \gamma\{E_{Nj}(V)\}) = \ln\Theta = \ln \sum_N \sum_j \; e^{-\beta E_{Nj}(V)} e^{-\gamma N}$$

$$\Rightarrow \; df = \left(\frac{\partial f}{\partial\beta}\right)_{\gamma,\{E_{Nj}(V)\}} d\beta + \left(\frac{\partial f}{\partial\gamma}\right)_{\beta,\{E_{Nj}(V)\}} d\gamma + \sum_N \sum_j \left(\frac{\partial f}{\partial E_{Nj}}\right)_{\beta,\gamma,\{E_{Nj}(V)\}} dE_{Nj}$$

Here we are keeping constant all E_{Nj} values except the one we are differentiating with.

$$\Rightarrow \; df = -< E > d\beta - < N > d\gamma + \beta < P > dV$$

$$\Rightarrow d(f + \beta < E > + \gamma < N >) = \beta\, d< E > + \beta < P > dV + \gamma\, d< N > \text{............(1)}$$

From thermodynamics for open system we get

$$T\,dS = dU + PdV - \mu\, dN \text{ …………..(2)}$$

Comparing equation (1) and (2)

$$\gamma = \frac{\mu}{k_B T} \text{ ………………(3)}$$

So, $S = \frac{<E>}{T} - \frac{<N>\mu}{T} + k_B \ln\Theta$ …………(4)

We know grand canonical partition function, $\Theta\,(V, T, \gamma) = \sum_N \sum_j e^{-\beta E_{Nj}(V)} e^{-\gamma N}$

Substituting the value of γ in the above expression we get

$$\Theta\,(V, T, \mu) = \sum_N \sum_j e^{-\frac{E_{Nj}(V)}{k_B T}} e^{\frac{\mu N}{k_B T}}$$

$$\Rightarrow \quad \Theta\,(V, T, \mu) = \sum_N Q(N, V, T)\, e^{\frac{\mu N}{K_B T}}$$

So Grand canonical partition function can be represented as a canonical partition function plus all possible values of N.

Gibb's energy $G = \mu N = U + PV - TS$

$$PV = \mu < N > +T < S > -< E >$$

$$\Rightarrow \quad PV = k_B \ln\Theta$$

Next we consider or next we will discuss micro canonical ensemble. In micro canonical ensemble number of particle, volume and energy is fixed. Since E is fixed

$$E_1 = E_2 = E_3 \ldots\ldots\ldots = E_\Omega$$

all systems are degenerate, very similar to the particle in a 3-d box, having N_x, N_y and N_z values are 1, 2, 1 or 2, 1, 1 or 1, 1, 2, so energy of these three states are the same, so they are degenerate.

So one would expect, $p_1 = p_2 = p_3 \ldots = p_\Omega$

$$\Omega(N, V, E) \Rightarrow \text{degeneracy}$$

In micro canonical ensemble N, V, E is fixed since, E is fixed, all energy values are same, so one would expect the probability of having all the states are the same. So we are going to prove that the probability of all the states are the same in micro canonical ensemble.

We know $$S = k_B \ln W = K_B \ln \frac{N!}{n_1!\, n_2!}$$

$$\Rightarrow \quad S = k_B \ln N! - k_B \ln n_1! - k_B \ln n_2! \ldots..$$

Applying Stirling's approximation,

$$\Rightarrow \quad S = k_B[N\ln N - N - \sum_i n_i \ln n_i + \sum_i n_i]$$

$$\Rightarrow \quad S = k_B[N\ln N - \sum_i n_i \ln n_i]$$

$$p_i = \frac{n_i}{N} \Rightarrow n_i = Np_i$$

$$S = k_B[N\ln N - \sum_i (Np_i) \ln(Np_i)]$$

$$\Rightarrow \quad S = k_B[N\ln N - \sum_i (Np_i) \ln N - \sum_i (Np_i) \ln p_i]$$

$$\Rightarrow \quad S = k_B[N\ln N - N\ln N \sum_i p_i - N \sum_i p_i \ln p_i]$$

$$\Rightarrow \quad S = k_B[N\ln N - N\ln N - N \sum_i p_i \ln p_i] \qquad [\sum_i p_i = 1]$$

$$\Rightarrow \quad S = \quad Nk_B \sum_i p_i \ln p_i$$

Now the statistical entropy,

$$S = -k_B \sum_{j=1}^{\Omega} p_j \ln p_j$$

$$\Rightarrow \quad ds = -k_B \sum_{j=1}^{\Omega} d(p_j \ln p_j)$$

$$\Rightarrow \quad ds = -k_B \sum_{j=1}^{\Omega} dp_j \,(\ln p_j + 1)$$

For an isolated system, at equilibrium, is one of maximum entropy, this we can learn from second law of thermodynamics. Basically we are now maximizing entropy. So,

$$ds = -k_B \sum_{j=1}^{\Omega} dp_j \,(\ln p_j + 1) = 0$$

Now we will simplify above expression like we have the constant

$$\sum_{j=1}^{\Omega} p_j = 1 \quad \text{or} \quad \sum_{j=1}^{\Omega} dp_j = 0$$

$$\Rightarrow \; dp_1 + \sum_{j=2}^{\Omega} dp_j = 0$$

$$\Rightarrow \; dp_1 = -\sum_{j=2}^{\Omega} dp_j$$

Now, if we use this expression in above expression of ds we get

$$0 = ds = -k_B \, dp_1(\ln p_1 + 1) - k_B \sum_{j=2}^{\Omega} dp_j \,(\ln p_j + 1)$$

$$\Rightarrow \quad -k_B \sum_{j=2}^{\Omega} dp_j \,(\ln p_j - \ln p_1) = 0$$

$$\Rightarrow \quad \ln p_j - \ln p_1 = 0 \qquad \text{as } dp_j \neq 0$$

$$\Rightarrow \quad p_j = p_1$$

So we get $p_j = p_1$, and this is valid for all possible values of j. Thus, we can write

$$p_1 = p_2 = p_3 \ldots = p_\Omega$$

this is known as postulates of equal a priori probabilities which says, for an isolated system in equilibrium, all microscopic states corresponding to the same set of a macroscopic observables are equally probable.

We have $\sum_{j=1}^{\Omega} p_j = 1$

$$\Rightarrow \quad p_1 + p_2 + p_3 \ldots + p_\Omega = 1$$

Since $p_1 = p_2 = p_3 \ldots = p_\Omega$

$$\Omega p_j = 1$$

$$\Rightarrow \quad p_j = \frac{1}{\Omega(N,V,E)}$$ this is micro canonical distribution function

Now, we arrived at the expression that $p_1 = p_2 = p_3 \ldots = p_\Omega$ by maximizing W or in other way in order to have the maximum entropy the probability of the all states must be equal. We simply calculate by considering 3 or 4 hypothetical systems.

We will consider a system with 4 states

Case-I : $p_1 = p_2 = p_3 = p_4 = \frac{1}{4}$

Case-II : $p_1 = \frac{1}{2},\ p_2 = \frac{1}{4}\ , p_3 = \frac{1}{8},\ p_4 = \frac{1}{8}$

For Case-I, $S_1 = -k_B \sum_{j=1}^{\Omega} p_j \ln p_j$

$$S_1 = -k_B[p_1 \ln p_1 + p_2 \ln p_2 + p_3 \ln p_3 + p_4 \ln p_4$$

$$S_1 = -k_B[4 \times \frac{1}{4} \ln (\frac{1}{4})] = k_B \ln 4$$

For Case-II, $S_2 = -k_B[\frac{1}{2} \ln (\frac{1}{2}) + \frac{1}{4} \ln (\frac{1}{4}) + \frac{1}{8} \ln (\frac{1}{8}) + \frac{1}{8} \ln (\frac{1}{8})]$

So we get $S_1 > S_2$

Now, we can calculate different thermodynamical quantities like S

$$S = -k_B \sum_{j=1}^{\Omega} p_j \ln p_j$$

$$\Rightarrow \quad S = -k_B \sum_{j=1}^{\Omega} \frac{1}{\Omega} \ln (\frac{1}{\Omega})$$

$$\Rightarrow \quad S = -k_B \ln \Omega(N, V, E)$$

Next, we can also calculate average pressure.

$$dU = TdS - PdV$$

since $dU = 0$, $TdS = PdV$

So, $P = T\left(\frac{\partial s}{\partial V}\right)_{E,N} = k_B T\left(\frac{\partial \ln\Omega}{\partial V}\right)_{E,N}$

We can also calculate enthalpy H like this.

Enthalpy $H = \langle E\rangle + \langle P\rangle V = \langle E\rangle + k_B T\left(\frac{\partial \ln\Omega}{\partial V}\right)_{E,N}$

Helmholtz free energy $A = < E > -TS = < E > - k_B T\,\partial\ln\Omega$